

Electrically tunable block copolymer photonic crystals with a full color display

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Electrically tunable full color display photonic crystals (PCs) made of a thin film of block copolymer, polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP), have been developed. The phase separation of PS and P2VP blocks leads to a one-dimensional periodic lamellar structure parallel to the surface of the thin film. In a solvent mixture of water and ethanol, each P2VP layer is swollen and partially charged. Applying a low voltage (<2.5 V) to such a thin film can lead to the repeatable expansion or contraction of each P2VP layer, depending on the direction and strength of the electrical potential. Such a variation of the lamellar periodicity leads to a full color display over a wide range from ultraviolet to near infrared. The advantages of such PCs are their facile preparation, low driving voltage and good durability, which make them potentially useful in information technologies.

Introduction

Photonic crystals (PCs) are a new class of materials with a periodic variation of dielectric constant. They can be used to manipulate and control light because their photonic band gap forbids the propagation of electromagnetic waves in a certain frequency range.^{1,2} Therefore, they exhibit non-bleachable structural color. Those PCs with a tunable color in the visible and near infrared regions have found applications in optical/memory devices and chemical/biochemical sensors.^{3–9} One of the focuses in this active research field is to develop PCs with a full color reflective display because they play a critical role in the development of high quality electronic papers and other information materials. In principle, one can achieve such a property by altering their periodicity and/or dielectric constants in response to an electrical, magnetic, or other stimulus. It was reported that PCs made of a thermally responsive poly(*N*-isopropylacrylamide-*co*-methacrylic acid) hydrogel could exhibit a full color spectrum.¹⁰ Another example is PCs made of colloidal super-paramagnetic magnetite nanocrystals with magnetically tunable stopbands covering the entire visible spectrum.¹¹

In practice, electrically responsive PCs are more useful and workable. Up to now, only limited work related to electrically tunable photonic crystals have been reported. Song *et al.* showed that applying an electrical field could make polypyrrole inversed opals change color, conductivity and wettability, but not over the entire color range.¹² Ozin *et al.*¹³ reported the first electrically tunable full color photonic crystal made of a polyferrocenyldisilane gel/silica opal composite with a reversible expanding and contracting lattice. Recently, they used a complicated procedure to develop some fast responsive polyferrocenylmethylvinylsilane and polyferrocenyldivinylsilane inverse gel opals.¹⁴

It is known that block copolymers can form periodic lamellae, hexagonally packed cylinders and double-gyroid microdomain structures depending on the volume fractions of the blocks.^{15,16} Thomas *et al.*¹⁷ reported a facile procedure to fabricate one-dimensional photonic crystals from a ternary blend of a diblock copolymer and two homopolymers. Recently, they reported that quaternized polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) with a one-dimensional periodic lamellar structure could form photonic crystals whose lamellar layer thickness and refractive index are adjusted by salt concentration. Such chemically tunable PCs can exhibit a large reversible optical change from ultraviolet to near infrared.¹⁸

In our current study, we have successfully developed electrically tunable full color photonic crystals based on a similar PS-*b*-P2VP block copolymer thin film with one-dimensional periodic lamellar structure. The idea for this study is based on the fact that the pyridine group in the P2VP block can be charged in solution so that the thickness of the P2VP layers or the periodicity of the lamellar film can be electrically adjusted. Our results confirm our original proposal and reveal that such prepared PCs have advantages over other types of PCs because of their facile preparation, low driving voltage (1–3 V) and broad continuously tunable wavelength range from invisible ultraviolet to invisible near infrared.

Experimental section

Materials

Polystyrene-*b*-poly(2-vinyl pyridine) diblock copolymer (PS-*b*-P2VP) was purchased from Polymer Source. The number average molar mass (M_n) of both PS and P2VP blocks is 1.90×10^5 g mol⁻¹. The polydispersity index (M_w/M_n) is 1.10. Ethanol and chloroform (Sinopharm) as well as propylene glycol monomethyl ether acetate (Aladdin) were used as received without further purification.

Lamellar film preparation

Each film was prepared on an indium tin oxide (ITO) glass with a KW-4A spin coater (CHEMAT Technology, Inc), starting

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from a 5 wt% PS-*b*-P2VP solution in propylene glycol monomethyl ether acetate. After the solution was uniformly dropped on the ITO glass surface, it was spun at 3000 rpm for 15 s. Then more PS-*b*-P2VP solution was added and spun at 500 rpm for at least 75 s. Such prepared films were annealed in chloroform vapor at 58 °C for 24 h. The thickness of the film was mediated by the concentration of the polymer solution and the speed of spin coating. Generally, the thickness of the film increases with concentration but decreases with the speed of spin coating. In the present case, the concentration was 5 wt%.

Measurements

A simple two-electrode electrochemical cell was used. The film on ITO served as the working electrode and another bare ITO plate was used as the counter electrode. The electrodes were separated by a rubber O-ring. The electrical potential dependent reflective spectra were recorded on a UV/Vis spectrophotometer (Unico 2802PCS) in the transmission mode. The morphology of the lamellar film was observed using a JEOL2100 high-resolution transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. Specimens for TEM were cut from the lamellar film and fixed in epoxy resin (Epon 812). Ultrathin cross-sections (*ca.* 60 nm) prepared with an ultramicrotome Ultracut E (Cambridge Instruments) were transferred to TEM grids and sputtered with a thin carbon layer to enhance the resistance of the sample to the electron beam. The specimens were stained with iodine vapor before the TEM experiment. The pH of the solvent mixture was measured on a Mettler Toledo 320 pH meter.

Results and discussion

A transmission electron microscopy (TEM) image of one of the photonic crystals in the dried state is shown in Fig. 1. Clearly, it has a well-defined lamellar microstructure with PS and P2VP layers parallel to the substrate, where dark layers are iodine-

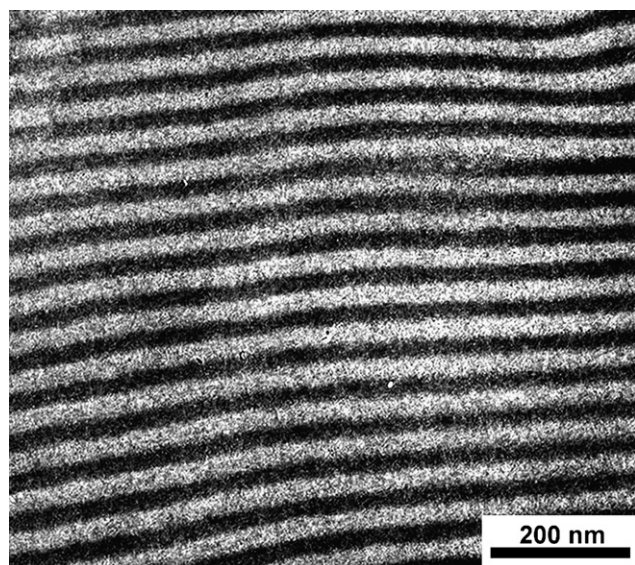


Fig. 1 TEM image of a PS-*b*-P2VP film (photonic crystal) stained with I₂ vapor.

stained P2VP domains. The periodicity is ~60 nm and the PS and P2VP layers have a similar thickness of ~30 nm. The dried film has a thickness of 2–4 μm so that each film has 60–140 layers.

Different electrical potentials were applied to the cell *via* two electrodes connected to a power supply. The cell was filled with a mixture of water (Milli-Q) and ethanol and sealed with epoxy. Note that the peak position of the reflected light is a function of the solvent composition. In a preliminary experiment, we found that the reflective peak shifts toward a longer wavelength (red) when the ethanol content increases because ethanol is a better solvent for P2VP in comparison with water. Each P2VP layer swells more as the ethanol content increases so that the lamellar periodicity also increases, but the refractive index of the P2VP decreases. Hereafter, all the results reported are from the 1 : 1 (v/v) mixture of water and ethanol.

Fig. 2 shows how the wavelength of the reflective peak gradually increases with the applied voltage. It is clear that when a positive potential is applied, the reflected light changes from blue ($\lambda_{\text{max}} = 470$ nm) to red ($\lambda_{\text{max}} = 633$ nm), leading to a full color display. It should be stated that the reflective peak even shifts into the near infrared region with its high order Bragg peaks in the visible region. Note that the optical quality of the film is low. This is because the film is relatively thin.¹⁹ When the thickness of the dry film is less than 1 μm, a dull color is observed. However, the color becomes much brighter when the film in the dry state is thicker than 2 μm. The voltage dependence of the peak wavelength is shown in the inset of Fig. 2, indicating a continuum of the accessible color over a very narrow voltage range of 0.0–2.5 V. The pH value of the solvent mixture is 6.2 since only ~2 mol% of the pyridine groups are charged in the solvent mixture. When a voltage is applied to the anode, each positively charged P2VP layer in the film is driven away from the anode, leading to the expansion of the film. It is known that the refractive indices of PS and P2VP in the dry state are 1.59 and 1.62, respectively. When P2VP layers are swollen by a solvent with a refractive index of ~1.34 to 1.35, the refractive index of the layer will decrease. Here, the refractive index of the P2VP layer is ~1.41 to 1.43 with a swelling ratio of 3–4. Such a result has been reported before.¹⁸ The swelling of each P2VP layer increases the lamellar periodicity and the refractive index contrast between the

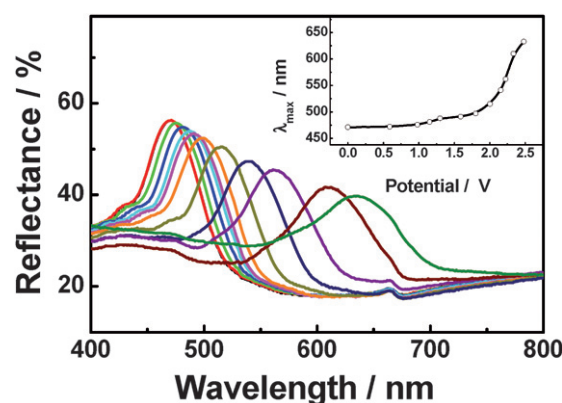


Fig. 2 Electrical potential dependence of the reflective spectrum of a PS-*b*-P2VP thin film (photonic crystal), where the inset shows the voltage dependence of the first Bragg peak position (λ_{max}).

PS and P2VP layers. This is why the reflective peak exhibits a red shift. Clearly, there is an obvious shift when the applied voltage is above ~ 1.5 V. As we know, P2VP chains entangle with each other at a low swelling ratio. When the applied potential reaches the critical value (~ 1.5 V), the chains begin to stretch and undergo some disentanglement, leading to an obvious red shift. It should be emphasized that the low driven voltage (< 2.5 V) can effectively avoid some side reactions in the solution mixture and reduce the energy consumption. The stretching and entanglement of P2VP also relate to the solvent quality. When the solvent leads to more disentanglement, a lower driving voltage is required. Using a mixture of acetonitrile and water, we can further lower the driving voltage to 1.2 V to cover the entire visible range. In comparison, the acetonitrile–water mixture is much more toxic than the ethanol–water mixture to the photonic crystal.

Fig. 3 shows that a switching of the applied voltage between -2.1 and $+2.5$ V leads to a reversible change in the position of the reflective peak or the current, where each data point was collected 15 min after applying the voltage to ensure that the mixture had reached its equilibrium state. Our results reveal that there is no visible hysteresis, which is important if the film is to be used for any electronic display devices. Note that the current is very low because of the low conductivity of the solvent mixture and because the P2VP block is only partially charged, which also explains why the stretching kinetics is slow in Fig. 4. The estimated power consumption for each cycle is only ~ 30 μ W.

The shifting kinetics of the reflective peak position after a positive voltage of 2.5 V is applied to the thin film is shown in Fig. 4. It shows that the reflective peak first shifts from 430 to 640 nm within ~ 15 min and then dramatically slows down before it reaches 660 nm over a long time. As discussed before, the shift is due to the increase of the periodicity, *i.e.*, the stretching of each partially charged P2VP block, and the decrease of the refractive index of each P2VP layer. Such a stretching has to overcome the conformational entropic elasticity that increases with the degree of deformation. This is why the variation of the peak position ($\lambda(t)$) *versus* time follows an exponential curve (dashed curve) of $[\lambda(t) - \lambda_\infty]/(\lambda_0 - \lambda_\infty) = \exp(-t/\tau)$, as shown in Fig. 4, where λ_0 , $\lambda(t)$ and λ_∞ are the positions of the reflective peak at $t = 0$, t

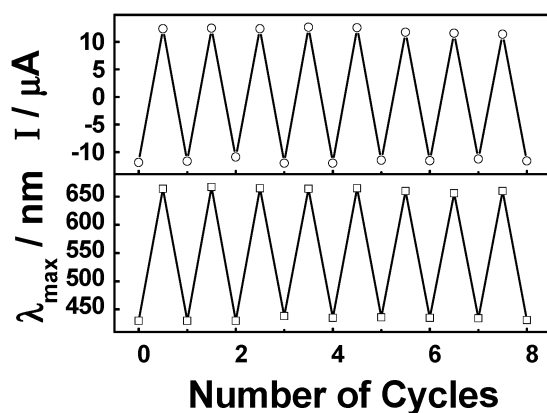


Fig. 3 Electrical potential (V) dependence of the first Bragg peak position ($\lambda_{\max}$) and electrical current (I) between two electrodes of a PS-*b*-P2VP thin film (photonic crystal), where V is switched between -2.1 and $+2.5$ V.

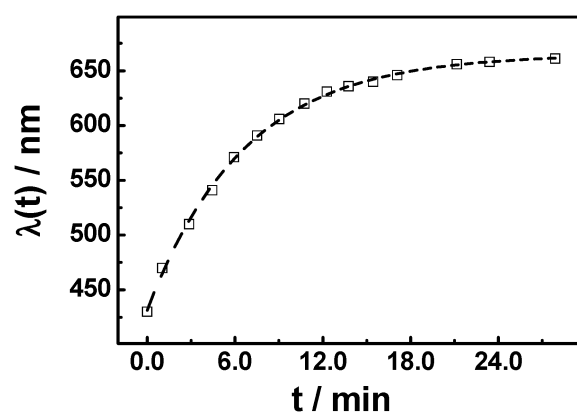


Fig. 4 Time dependence of the first Bragg peak position ($\lambda(t)$) of a PS-*b*-P2VP thin film (photonic crystal) after application of a positive voltage of 2.5 V.

and ∞ , respectively; t is the time after which the voltage was applied and τ is the characteristic responsive time. The fitting (dashed curve) in Fig. 4 reveals that $\tau = 6.6$ min. When the electrical stretching force is balanced by the entropic elastic force, the increase of the lamellar periodicity stops and so does the

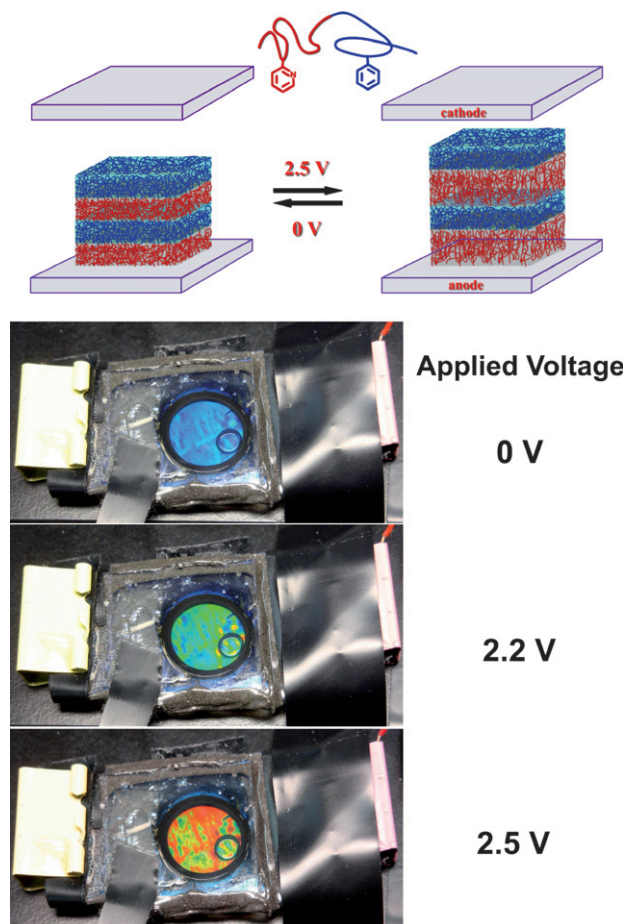


Fig. 5 Schematic representation of the potential induced conformational change of a PS-*b*-P2VP thin film (photonic crystal) and photographs of the film at different applied voltages.

shifting of the reflective peak. As stated above, the response is slow because the P2VP block is partially charged. In our preliminary experiment, we found that the response becomes much faster after the P2VP block is quaternized.

Fig. 5 schematically shows the potential induced conformational change of a PS-*b*-P2VP thin film and photographs of the film at different applied voltages. The display area inside the rubber O-ring was about 1 cm² and a bubble in the cell can be found which shows that the liquid reservoir is surrounded. Photographs were taken under an 18 W desk lamp which can be considered normal lighting conditions.

Conclusions

In summary, we have successfully developed a new type of electrically tunable photonic crystal with a full color display, low switchable voltage and good durability. Such crystals are potentially useful in information techniques.

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